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ABSTRACT

Four-carbon and higher molecular weight olefins can be quantitatively determined in the gas phase by reaction with p-dimethylaminobenzaldehyde in concentrated sulfuric acid, heating at 100°, and measurement of the absorbance at 500 mμ. The absorptivities are such that 0.1 ppm or less of gaseous olefins can be determined. Interference by formaldehyde is appreciable. Excess amounts of aromatic hydrocarbons and phenols interfere somewhat in the procedure. Simple methods for removing possible interferences in gas mixtures are discussed. The method has been applied to the analysis of automobile exhaust and diluted irradiated exhaust mixtures.

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Various effects associated with "smog" on the West Coast of the United States, including eye irritation and plant damage, have been attributed to the photooxidation of mixtures of olefins and nitrogen dioxide. Consequently, diverse analytical methods are needed to analyze for olefins both in the atmosphere and in combustion gases. Several instrumental methods, including gas chromatography, infrared spectroscopy and mass spectrometry, have been applied successfully to the analysis of combustion gas olefins and, to a lesser extent, to atmospheric olefins. However, a need exists for other methods sensitive enough to determine <u>total</u> olefins in both combustion gases and the atmosphere.

Several chemical methods for olefins have been investigated for application to the trace analysis of olefins (2,4,15,17). Most of these methods have lacked sufficient sensitivity for convenient analysis of atmospheric concentrations of olefins. Certain other limitations have existed in terms of interferences, variation in response of individual olefins, simplicity and ease of application.

The present colorimetric method for olefins is more sensitive than the previous ones. Olefin concentrations down to about 0.1 ppm by volume can be determined quantitatively using reasonable sampling periods. The experimental procedure is simple and rapid. The colored product formed is stable for several hours.

The use of an aromatic aldehyde as a reagent for the analysis of olefins in a strongly acidic solvent appeared promising to the present investigators. Previous workers have studied in some detail the color reactions between aromatic aldehydes and alcohols in concentrated sulfuric or hydrochloric acid (Komarowsky Reaction) (6,7,9,14,15,20). Both dehydration (6,15) and aldol condensation (7) have been suggested as steps in the reaction. It seemed possible, as suggested (15), that the alcohols and olefins react with the aromatic aldehyde through similar intermediate species. Preliminary measurements on the reaction products of olefins with a number of aromatic aldehydes in concentrated sulfuric acid indicated that p-dimethylaminobenzaldehyde is a very satisfactory reagent. This aldehyde was used in the subsequent work.

When p-dimethylaminobenzaldehyde reacts with olefins in concentrated sulfuric acid under appropriate conditions, colored products are obtained which usually have their absorption maxima or shoulders at 500 mμ. The new method is particularly applicable to the analysis of total four-carbon and higher molecular weight olefins.

EXPERIMENTAL DETAILS

The sources and purities of the olefins used, and of the substances tested as possible interferences, have been discussed elsewhere (4). In the preliminary work, olefins were prepared in sulfuric acid solution as described previously (4).

In the bulk of the work done, individual hydrocarbons and mixtures of hydrocarbons were introduced into aluminized Scotchpak bags or Mylar bags by means of microsyringes and diluted to an appropriate volume (20 to 100 liters)(5).

The gaseous hydrocarbon samples were injected from a microsyringe through a septum cap on a glass T and flushed into the bag with air. Liquid samples were injected from microsyringes through a septum cap on a glass T into an evacuated cylindrical flask, and the vapor in the flask and associated glass tubing then was flushed into the bag with air. Microsyringes of 1 and 10 µl capacities were used for the liquid samples, while syringes of 30 µl to 10 ml capacity were used for the gas samples. The gas or vapor mixtures in air prepared by this method had hydrocarbon concentrations ranging from 0.2 to 500 ppm by volume in total volumes ranging from 20 to 150 liters. Diffusion cells were used to obtain trace concentrations of the vapors of formaldehyde and of 1-hexene in air (1).

The p-dimethylaminobenzaldehyde reagent is prepared by dissolving 10% by weight of DAB (mp 73-75°) in glacial acetic acid. The resulting solution is greenish-yellow in color. The stability of this solution is excellent for several weeks. The solutions are stored in glass-stoppered bottles covered with aluminum foil.

Recommended Procedure for Gas Sampling. -- The volume of gas desired is collected in a bubbler containing the reagent in sulfuric acid. This collection solution is prepared by adding 0.25 ml of the 10% DAB in glacial acetic acid to 20 ml of concentrated sulfuric acid. Twenty milliliters of this solution is placed in each bubbler. Conventional cylindrical midget bubblers can be used at flow rates not exceeding 0.3 or 0.4 liters/minute. Higher flow rates cause excessive foaming. Bulb type bubblers afford a larger vapor space above the solution than the midget bubbler and can be used at flow rates up to at least one liter/minute.

After collection of the gas sample, the collecting solution is transferred to a test tube, heated at 100° for 20 minutes in a water bath and then cooled. The absorbance is read at 500 mμ and will be stable (± 5%) for at least two or three hours. A few measurements indicated satisfactory stability overnight.

Calculations. -- For samples containing from about 5 to 200 ppm by volume of C_4 and higher olefins, the concentration of olefins in μg per liter is given by the following expression:

$$\text{μg/liter of } C_4 \text{ and higher olefins as 1-butene} = \frac{A(500\ m\mu) \times \text{ml. reagent} \times 10}{\text{liters of air sampled}}$$

At olefin concentrations below 5 ppm by volume, the same expression applies, except that a factor of 7 should be used rather than 10. These factors are the reciprocals of the absorptivities for 1-butene. However, the absorptivities for 1-butene are within ± 10 to 20% of the average absorptivities for such applications as automobile exhaust olefin analysis. The concentration of olefins in μg per liter can be converted to parts per million by volume, if the average carbon number of C_4^+ olefins in the sample is known.

Calibration. -- The dilute gas or vapor mixtures discussed previously must be used for calibration. Pure gases or liquid olefins will not give equivalent results. For example, the most dilute mixture of a liquid 1-hexene in sulfuric acid which can be prepared accurately will give an absorptivity about 50% lower than the same concentration of olefin in the reagent collected from a vapor mixture of 1-hexene in air. The calibration mixture may be made up in plastic bags, a glass flask, or generated from a diffusion cell. If a gaseous olefin is used, 1-butene is recommended. If a liquid olefin is used as a dilute vapor, 1-hexene can be used.

RESULTS

Selection of Aromatic Aldehyde. -- p-Dimethylaminobenzaldehyde was selected as the reagent in the procedure used only after the following aromatic aldehydes were tried in preliminary experiments: o-methoxybenzaldehyde, salicylaldehyde, p-nitrobenzaldehyde, m-nitrobenzaldehyde and p-diethylaminobenzaldehyde . None of the other aromatic aldehydes formed as strongly absorbing reaction products with olefins as did p-dimethylaminobenzaldehyde. 1-Hexene forms products with m-nitrobenzaldehyde and p-diethylaminobenzaldehyde which have absorption maxima one-half and one-third as intense respectively, as the product formed with p-dimethylaminobenzaldehyde. The other aldehydes react with olefins to form even more weakly absorbing products. On the basis of these results it was felt that p-dimethylaminobenzaldehyde was the aldehyde of choice.

Sulfuric Acid as a Collecting Medium. -- Concentrated sulfuric acid was chosen for use on the basis of results obtained on the 1-hexene product. The absorptivity decreased about 25% in 90% sulfuric acid compared to the absorptivity in concentrated acid. No absorption was detectable in the 500 mμ region when 80% sulfuric acid was used.

The olefin can be collected out of a gas stream or added directly to concentrated sulfuric acid. The p-dimethylaminobenzaldehyde (DAB) reagent is added later. Results obtained using this procedure for 1-butene, cis-2-butene, and isobutylene are given in Table I.

The long reaction period used in this procedure (Table I) is time-consuming. More significant are the large differences in absorptivities even among the butene reaction products. With the optimum ratio of reactants and

reaction time, isobutylene forms a product which absorbs six to seven times as much as the corresponding 1-butene product. Somewhat smaller differences in absorptivities exist between 1-butene and cis-2-butene and between cis-2-butene and isobutylene. Although data were not obtained on the 1,3-butadiene product in this procedure, data obtained using the procedures to be discussed later indicate that the 1,3-butadiene product would absorb about as strongly as the isobutylene.

These wide variations in reactivity among the olefins makes this procedure unacceptable for application to gas samples containing complex mixtures of olefins of initially unknown composition. For specific analyses involving a single reactive olefin such as isobutylene alone or mixed with other non-olefinic hydrocarbon components, this procedure may have applicability.

p-Dimethylaminobenzaldehyde-Sulfuric Acid as a Collecting Medium. -- Another procedure investigated involved the preparation of collecting solutions containing various ratios of DAB in glacial acetic acid to sulfuric acid. For example, a 1-to-4 solution is prepared by adding 5 ml of 10% DAB in acetic acid to 20 ml of concentrated sulfuric acid. The absorptivities listed (Table II) are based on µg of olefin per ml of the final reaction mixture, since the total volume of collecting solutions varied from 20.25 ml to 25 ml. The solution, after collection of the individual olefins from the air stream, are allowed to react for periods ranging from about 15 minutes to 2 hours, after which the absorbance is read at 500 mµ.

Again considerable difficulty was experienced in trying to obtain approximately equal absorptivities for the products of different types of olefins. The products of more reactive olefins such as isobutylene and 1,3-

butadiene, at all the DAB-to-sulfuric acid ratios and at all of the reaction times studied, always had much higher absorptivities than did olefinic species such as 1-butene or cis-2-butene. At DAB-H_2SO_4 ratios of 1/8, 1/20, 1/40 the propylene product has a small but by no means insignificant absorptivity. In combustion mixtures such as automobile exhaust, in which the propylene concentration far exceeds the concentration of individual higher olefins, this degree of reactivity for propylene would lead to considerable uncertainty in the analytical results.

This procedure may have possibilities in the analysis of the more reactive higher molecular weight olefins. At a 1/80 DAB-H_2SO_4 ratio, propylene, 1-butene and cis-2-butene products absorb very weakly, while isobutylene and 1,3-butadiene products form moderately strongly absorbing reaction products.

A variation of this procedure involved heating of the product formed at 100°, for varying times, then reading the absorbance. Some of the results obtained for the products formed by several olefins with DAB reagent are given in Table III.

At a 1/8 ratio of DAB to sulfuric acid, the propylene product absorbs a third to one-half as intensely as do the higher molecular weight olefins. All of the results obtained in the present work indicated that it would be very difficult, if not impossible, to adjust experimental conditions so that the propylene product would absorb as strongly as a higher molecular weight olefin. Consequently, conditions were sought which would reduce the intensity of absorption of the propylene product to a negligible level.

It was found that the use of a 1/80 ratio of DAB to sulfuric acid and a 15 or 20 minute heating period will reduce the absorptivity of the propylene

product to between 1 to 3% of the absorptivities at 500 mμ of the products of the higher molecular weight olefins. Similarly, the absorptivity of the ethylene product is only 1 or 2% of the absorptivities of the butenes and higher molecular weight olefins.

The absorptivities of the products of butenes and higher molecular weight olefins with DAB reagent fall into about a three fold range (Table IV). In adjusting experimental conditions, losses in overall intensities have occurred. Absorptivities two to three times greater than those obtained at the 1/80 ratio can be obtained at other ratios with the present procedure or with the procedures previously discussed. The use of the 1/80 ratio and a 15 or 20 minute heating period and the reading of the absorbance at 500 mμ appears to be the best compromise. Although some of the olefin products have maxima at 520 mμ, this wavelength is not used because the isobutylene and many of the products formed by five or six carbon olefins have low absorptivities at 520 mμ. The 1/40 ratio, a 15 minute heating period, and reading of the absorbance at 500 mμ is almost as satisfactory, except for the greater interference from propylene owing to the higher absorptivity of its product at this ratio.

It was desirable to check the static system used by a dynamic method (1). A significant loss of olefin, particularly liquid olefin, might result from a combination of vaporization losses in introducing the olefin into the evacuated glass flask used and by adsorption losses on the surfaces of the flask and the plastic bag. If so, a low absorptivity would result. Instead, when 1-hexene was generated from a diffusion cell, an absorptivity of 0.076 was obtained compared to the value of 0.085 μg^{-1} ml cm^{-1} obtained in the static system (Table IV).

The increase in the absorptivities with decreasing concentration of olefin in the gas mixture is most pronounced for the butene products and is much less marked for the pentene and hexene products. Gas volumes collected were varied as the olefin concentration of the gas mixtures changed so that the amount of olefin in the reagent solution did not vary significantly. Consequently, deviation from Beer's law is not responsible for this increase in absorptivities. Nor is this variation in absorptivity with gas phase olefin concentration due to differences in collection efficiency. One set of individual or average absorptivities must be used at olefin concentrations in the gas phase at about the 5 ppm level and below, and another at higher concentrations. The situation will be discussed in much more detail later in this work.

Nature of Absorption Spectra and Intensities of Products. -- The wavelength positions of the maxima and shoulders in the absorption spectra of the products of individual olefins with the p-dimethylaminobenzaldehyde reagent do not shift with increase in length of the heating period, but the overall intensities and the ratio of intensities of maxima to shoulders do vary. The intensities also vary with changes in ratio of DAB reagent to sulfuric acid volume (Table III).

The ethylene and propylene products have maxima at 520 mμ and shoulders at 500 mμ. The overall intensities are low, particularly at 1/40 and 1/80 dilution ratios.

Isobutylene forms a reaction product with an intense maximum at 500 mμ. Its absorption at 470 mμ occurs as a slight maximum rather than as a shoulder (Figure 1).

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The reaction products formed by 1-butene, cis- and trans-2-butene and 1,3-butadiene have absorption maxima at 520 mμ and shoulders at 500 mμ. The 1,3-butadiene reaction product has a maximum at 520 mμ which is about as intense as the maximum of the isobutylene product at 500 mμ (Figure I).

The absorption spectrum of the reaction product formed by most of the five and six carbon monoolefins with the reagent is rather diffuse. A broad, flat maxima usually occurs in the 490-500 mμ and 450-460 mμ region.

The intensity of the absorption of the 1-butene product at 500 mμ was shown to be linear with olefin concentration. When 2,6 and 16 liters of about 15 ppm 1-butene in air were collected in DAB reagent, the following absorbances were obtained after 15 and 20 minute heating periods: 0.43, 0.43; 1.31, 1.29; 3.41 and 3.30. Similarly data for 1,3-butadiene at the 1 ppm level also indicates that Beer's law is obeyed by the reaction products of the olefins with DAB reagent.

Collection Efficiencies. -- Individual olefins, hydrocarbon mixtures and exhaust gases at concentrations down to about 0.2 ppm have been passed through reagent solution in bubblers with 80 to 90% of the olefin collected in the first bubbler at flow rates up to 500 ml/minute and for total volumes up to 30 liters. At flow rates of 1000 ml/minute, and total volumes to 60 liters, the collection efficiency decreases somewhat, with 80 to 85% of the olefin retained in the first bubbler in the collection train. Conversely, samples of only a few liters can be collected at efficiencies over 90% in a single bubbler, if flow rates of only 200 ml/minute are used.

Aliphatic Hydrocarbon Mixtures. -- It was desirable to analyze a series of hydrocarbon gas mixtures over a wide range of olefin concentrations. These

gas mixtures were prepared by diluting Phillips hydrocarbon mixtures with air to give olefin concentrations ranging from 0.2 to 100 ppm by volume of total olefins. The Phillips No. 36 mixture used had the following composition in mol. percent: 1-butene, 13.87; trans-2-butene, 9.00; cis-2-butene, 6.10; isobutylene, 9.15; 1,3-butadiene, 0.02; n-butane, 32.04, isobutane, 29.80 and neopentane, 0.02. The Phillips No. 37 mixture used had the following composition in mol. percent: 1-butene, 17.04; trans-2-butene, 21.92; cis-2-butene, 18.91; isobutylene, 7.04; 1,3-butadiene, 17.83; n-butane, 14.03; and isobutane, 3.23. The total hydrocarbon and olefin concentrations, the observed and calculated olefin concentrations are given in Table V. The calculated absorbances are obtained by summing the absorbances for the individual olefins for the same gas volume and concentration. It was assumed that the 1 ppm calibration data for individual olefins could be applied in the calculations at total olefin concentrations of 0.2 and 1.0 ppm. Similarly, it was assumed that the 12.5 ppm calibration data could be applied in the calculations at total olefin concentrations of 10 and 100 ppm.

The calculated olefin concentrations are in good agreement with the true olefin composition. Only one calculated value differs from the true values by more than 10%. The average difference between calculated and true olefin concentrations after 20 minutes heating is 5.5%, while the average difference between calculated and true values for olefins after 15 minutes heating is 3.5%.

It is interesting to observe that although at the 0.2 and 1.0 ppm total olefin concentrations the individual olefins exist at concentrations as low as 0.02 ppm, use of the 1 ppm olefin calibration data gives good agreement. On

the other hand, when the 1 ppm calibration data (Table IV) is applied to the 12 ppm hydrocarbon mixtures, the calculated values are much too high. For example, use of the 1 ppm calibration values for the 12 ppm hydrocarbon mixture (10 ppm olefin), results in an absorbance of 0.67 compared to an experimental value of 0.48 for the 15 minute heating period.

These results indicate that the 1 ppm calibration data for individual olefins should be applicable to olefin analyses at atmospheric levels. Similarly, the calibration data for the individual olefins in the 9-13 ppm range should be applicable to the olefin levels found in combustion gases.

It can be concluded that olefins react independently of each other. The paraffins present in the mixture do not interfere with the olefin analysis. Consequently, the present procedure can readily be applied to analyzing for trace quantities of olefin in various mixtures of such aliphatic hydrocarbons.

Reactions of Other Species with the Reagent. -- Various classes of compounds may interfere by reaction with the colorimetric reagent. This is the type of interference considered in this section. Other species besides olefins may react with the DAB reagent to form products which have absorption maximum in the 500 mμ region. Some species may also react with DAB to form products with absorption maximum in the ultraviolet, but the absorption bands may be sufficiently intense so that the tails of these bands absorb significantly in the 500 mμ region. Other types of interference can occur by direct reaction of some classes of compounds directly with the olefins in the strongly acidic medium used. This type of interference is important and it will be discussed in detail in several of the following sections.

Nitric oxide, nitrogen dioxide, sulfur dioxide, paraffins, acetylenes, benzene, toluene, o-xylene, p-xylene, saturated aldehydes and ketones, aliphatic acids, and some simple phenols do not react with dimethylaminobenzaldehyde reagent sufficiently to produce products with any significant absorption in the 500 mμ region. Toluene, o-xylene and p-xylene do react sufficiently to form products which have weak absorption maxima in the 425 mμ region.

Although methanol and ethanol are unreactive, and the propanols react only slightly with DAB reagent, the butanols and higher alcohols are very reactive. Tert.-butyl alcohol reacts with DAB reagent to form a product which has an absorption spectra with absorption maxima at 500 and 470 mμ as does the isobutylene product. The absorptivity of the tert.-butyl alcohol product at 500 mμ is quite close to that of the isobutylene product also. Other higher alcohols and esters also form colored products with DAB reagent. However, there is no indication of significant concentrations of higher alcohols in combustion sources ([8]).

While the other simple aromatic hydrocarbons tested reacted to form light yellow products, m-xylene forms an intensely yellow product of DAB reagent with an absorption maximum at 425 mμ with an absorptivity of about 0.01 μg^{-1} ml cm^{-1}. The tail of this absorption band has an absorptivity of only 0.002 μg^{-1} ml cm^{-1} at 500 mμ. Consequently, the interference of aromatic hydrocarbons owing to their reaction with DAB reagent is very small.

A vapor sample of m-cresol at about 10 ppm in air when passed through DAB reagent reacted only slightly. An absorptivity of about 0.01μg^{-1} ml cm^{-1} was obtained for the m-cresol product at 500 mμ. Other simple phenols might

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be expected to be even less reactive. Polyhydroxy phenols such as resorcinol and phloroglucinol will react to form products which absorb in the 500 mμ region (13).

Although saturated aldehydes and ketones are unreactive with DAB reagent, an unsaturated aldehyde such as acrolein might be expected to form an absorbing product with DAB reagent. However only a weakly absorbing product is formed with a weak maximum at about 375 mμ. At 500 mμ the acrolein product has an absorptivity of only 0.01 μg^{-1} ml cm^{-1}.

Thiophene has been determined by reaction with dimethylaminobenzaldehyde (12). In the present procedure thiophene reacts with DAB reagent to form a strongly absorbing product with a maximum at 390 mμ. At 500 mμ the thiophene product has an absorptivity about equal to that of the less intensely absorbing olefin products.

Olefin-Acetylene Mixtures. -- To test the possible interference of acetylene through direct reaction with the olefins, a gas mixture containing 100 ppm of olefin obtained by diluting mixture 37 and 200 ppm of acetylene was analyzed. Absorbances of 0.47 and 0.44 were measured when 0.25 liter of this mixture was passed through DAB reagent and the solutions are heated for 15 and 20 minutes at 100°. A mixture of 100 ppm of the same olefins in the same proportions when analyzed under the identical conditions gives absorbances of 0.47 and 0.43. Consequently, no interference with the analysis of the olefins is observed owing to a two-fold excess of acetylene.

Olefin-Aromatic Hydrocarbon Mixtures. -- It already has been reported that some aromatic hydrocarbons react to a small extent with the DAB reagent. In addition, aromatic alkylation might be expected to occur in sulfuric acid when

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olefins and aromatic hydrocarbons coexist in the vapor mixture. The results obtained for vapor mixtures containing 1-butene, isobutylene or 1,3-butadiene and single aromatic hydrocarbons including benzene, toluene, p-xylene, o-xylene, or m-xylene are given in Table VI. The data given is for a 1 to 80 ratio and the average results for 15 and 20 minute heating periods.

The aromatic hydrocarbons used had only a small effect on the extent of formation of the 1-butene reaction product. It is doubtful that the small differences observed between the concentrations obtained from analysis and the actual concentrations really are significant.

All of the aromatic hydrocarbons react somewhat with isobutylene in the reagent solution. The interference of toluene, p-xylene and o-xylene at a four-fold excess over the isobutylene amounts to 25 to 30%. The m-xylene reacts even more with the isobutylene in sulfuric acid (Table VI).

The 1-butene and isobutylene are representative of monoolefins of widely differing reactivity in many types of reactions. The degree of interference by aromatic hydrocarbons with these two olefins should give a good indication of the overall interference situation. If so, it would be expected that the aromatic interference in a mixture containing a number of aromatic hydrocarbons and many types of higher molecular weight olefins would be small but significant.

Aromatic hydrocarbons are attacked quite vigorously by 1,3-butadiene in the reagent solution (Table VI). If 1,3-butadiene alone is determined in combination with a four-fold excess of a mixture of aromatic hydrocarbons, an analysis would give only about one-half of the actual concentration.

The significance of this interference depends largely on the aromatic hydrocarbon and olefin composition and ratio in particular gas samples. Data to be discussed in detail later in this work on some automobile exhaust effluents indicates only a moderate interference for the samples analyzed.

A two-foot column of 20% carbowax 1540 on firebrick at room temperature will retain hydrocarbons much longer than olefins of equal carbon number. Several runs with an isobutylene-m-xylene mixture using such a column resulted in the removal of almost all of the aromatic hydrocarbon without loss of the olefin. Similar results were observed using this column with a vapor containing a mixture of six to nine carbon olefins and the xylenes. No loss of olefins up to nonenes should occur in the treatment of small samples. The column is particularly useful for removing aromatic hydrocarbons from relatively small volume samples. With the large samples needed below 10 ppm of olefin, considerable breakthrough of the aromatic hydrocarbons will occur.

A bubbler containing propylene glycol was found to be capable of removing m-xylene and presumably other aromatic hydrocarbons. The interference of m-xylene even with 1,3-butadiene can be largely eliminated by the use of a bubbler containing propylene glycol preceding the bubbler containing the DAB reagent. The sample rate should not exceed 200 ml/minute, if breakthrough of the aromatic is to be avoided. A complete study of the ability of various glycols and related oxygenates to remove aromatics was not made. It is possible that a more efficient solvent can be found which will permit the use of appreciably higher flow rates in cleaning the aromatics out of samples.

Olefin-Phenol Mixtures. -- A vapor mixture containing 12.5 ppm of 1,3-butadiene and 25 ppm of m-cresol was analyzed to determine the possible interference

of phenols in the olefin analysis. Five determinations each, using 15 and 20 minute heating periods, gave a concentration of 13.6 ppm for the 1,3-butadiene compared to the concentration as prepared of 12.5 ppm.

A second vapor mixture was prepared containing Phillips No. 37 diluted to 100 ppm of olefin and 50 ppm of m-cresol. This mixture analyzed at about 90 ppm olefin.

The variations, ± 10%, in the olefin contents as analyzed from the olefin concentrations as prepared, are small, but probably real. Since m-cresol was chosen as an example of a particularly reactive phenol, and the butadiene and olefin mixture chosen also are highly reactive, the mixtures used represent unfavorable analytical situations. Even so, the interference from phenols does not appear to be serious in most analytical situations of interest.

If a considerable excess of vapor phase phenols exist along with the olefins, then removal of the phenols may be necessary. The carbowax column discussed previously should remove phenols effectively. A bubbler or impinger containing water or alkaline aqueous solution should be effective in removing phenols from air samples containing large amounts of phenols prior to collection of olefin in the DAB solution.

Olefin-Formaldehyde Mixtures. -- Vapor mixtures containing formaldehyde at 20 to 40 ppm and olefin also at 20 and 40 ppm prepared by diluting Phillips No. 37 and 40 were analyzed for their olefin content. The mixtures containing formaldehyde at a two-fold excess over the olefins prepared from Phillips No. 40, analyzed at 30 to 50% higher than the olefin content as prepared. The mixtures containing olefins from Phillips No. 37 at one part of formaldehyde to two

parts by volume of olefin and two parts formaldehyde to one part by volume of olefin analyzed at 50 to 100% higher than the olefin content as prepared. This type of intensification of the spectra has been discussed previously (2). Consequently, it is essential that the formaldehyde, unless present at much lower concentrations than the olefin, be removed from the sample being analyzed for olefin.

Ascarite, which was the most effective of several solid adsorbents tested, only removed 70% of the formaldehyde (2). The carbowax column discussed removed some formaldehyde, but was not very efficient. Water, aqueous bisulfite solutions, and aqueous hydrazinobenzothiazole solutions (21) were effective in removing most of the formaldehyde. Saturated aqueous bisulfite and hydrazinobenzothiazole solutions (21) had the highest efficiency for removal of formaldehyde diluted to 20 to 40 ppm in air. No significant loss of butenes or pentenes were observed in these aqueous solutions.

While formaldehyde alone does not react in sulfuric acid (2) other aldehydes have been shown to undergo condensations to form products which absorb between 255 and 275 mμ (2). The spectra of a 2-methyl-2-butene-acetaldehyde mixture in sulfuric acid shows no indication of the intensification of absorption found for olefin-formaldehyde mixtures owing to Prins type reactions (2). Consequently, other aldehydes will not interfere as markedly as formaldehyde. Since the higher aldehydes will be largely removed by the same solutions that remove formaldehyde, they should present no significant problem.

Olefin-Nitrogen Dioxide Mixtures. -- A gas mixture containing 5 ppm of 1-butene and 2 ppm of nitrogen dioxide was analyzed. The average absorbances after 15

and 20 minute heating periods were 0.69 and 0.67. The same quantity of 1-butene alone gave absorbances of 0.70 and 0.65. Consequently, no interference was detectable from the nitrogen dioxide. No gas phase reaction of the 1-butene with nitrogen dioxide was detectable over the three-hour period these materials were being sampled from a plastic bag. No serious interference by nitrogen dioxide was found in a vapor mixture containing 5 ppm of 1,3-butadiene and 15 ppm of nitrogen dioxide. Nitric oxide does not interfere significantly even in large excess. However, serious interference will occur if there is a large excess of nitrogen dioxide in the mixture.

Choice of Average Absorptivity. -- In many trace methods of analysis for whole classes of compounds such as aldehydes or olefins, the responses of individual members of the class vary widely. Two or three-fold ranges of absorptivities are common. Such ranges of response occur in applying 2,4-dinitrophenylhydrazine in alkaline solution to the colorimetric analysis of aldehydes and ketones (11), Schiff reagent to aldehyde analysis (10), and 3-methyl-2-benzothiazolone hydrazone reagent to aldehyde analysis (22). Both the molybdate method (16) and bromination method (17) for vapor phase olefins show such differences in reactivity of individual olefins.

These variations in response present no problem in analyzing a gas mixture containing only one olefin, or a mixture of olefins of approximately known relative composition. However, a real problem does exist when these methods of analysis are applied to samples containing an unknown proportion of various olefins. Several choices exist. The concentration can be expressed in terms of a single member of the class. Alternatively, equal weighting can be given to the absorptivities of individual olefins if data is available for

a fairly representative group of olefins. An average absorotivity based on equal weighting then can be calculated. Independent analytical data on the proportion of various species can be used to assign appropriate weightings for individual olefins and these weighted values then can be used to arrive at an average absorptivity. All of these alternatives will be discussed with respect to automobile effluent analysis.

Automobile Effluent Analysis. -- The reproducibility of the olefin method was tested on a one and a half part per million by volume of 1-butene sample injected into a 330 cubic foot chamber. Analyses made over a two hour period gave 1-butene contents of 3.78, 3.80, 3.88 and 3.78 μg/liter. A more severe test was made by making analyses on diluted automobile exhaust over a five hour period. The gas stream analyzed at 15.8, 15.3 and 15.9 μg/liter of higher olefins. Over a one month period a series of nine analyses during six runs gave olefin contents in the range of 13.6 to 15.9 μg/liter with an average value of 14.7 μg/liter and a standard deviation of 0.7 μg/liter. This deviation of about 5% represents not only sampling and analysis errors, but also error owing to variations in the automobile operation and dilution system. The same automobile and fuel were used in all of these runs. These data indicate that analyses by the DAB method have good reproducibilities.

One method for obtaining an average absorotivity is to use the gas chromatographic data available for individual four, five, and six carbon olefins to assign weighting for individual olefins. Gas chromatographic analyses were available on the exhaust from the combustion of a number of fuels of varying olefin content (17), diluted exhaust from the combustion of two of these fuels, and atmospheric analyses. The 10 to 13 ppm calibration data for individual olefins were multiplied by the concentration of the olefin, and the average

absorptivity was obtained by summing these products and dividing by the total olefin concentration. The absorptivities obtained using the 20 minute heating data ranged from 0.096 to 0.115 with an average absorptivity of 0.103 μg^{-1} ml cm^{-1}. This data indicates that the ratio of olefins varies only over a narrow range. Consequently, an average absorptivity of 0.10 μg^{-1} ml cm^{-1} should be applicable to automobile exhaust analyses using most fuels.

A different average absorptivity must be applied for diluted exhaust gases, and diluted, irradiated exhaust gases. The 1 ppm calibration data for olefins (Table IV) should be applicable. The appropriate gas chromatographic analyses available were used. The average absorptivities computed from these data ranged from 0.12 to 0.16 μg^{-1} ml cm^{-1} with an overall average of 0.14 μg^{-1} ml cm^{-1}.

An alternative to the use of the gas chromatographic analyses in the computation of average absorptivities, is the expression of the olefin content in terms of a single olefin. It proves convenient to use 1-butene as this olefin. The absorptivities for 1-butene at 12.5 and 1 ppm of 0.11 and 0.15 μg^{-1} ml cm^{-1} are quite close to the average absorptivities discussed above of 0.10 and 0.14 μg^{-1} ml cm^{-1}. If equal weighting is given to the olefins listed in Table IV (with estimates for some olefins at the 1 ppm level), average absorptivities of 0.12 and 0.16 μg^{-1} ml cm^{-1} are obtained. In view of this degree of agreement, the expression of the olefin content of unknown complex mixtures of olefins in terms of 1-butene appears to be an acceptable procedure.

A good test of accuracy of the DAB method is provided by analyses of diluted automobile exhaust. With such a sample the DAB method can only be judged by comparing it with another analytical method. Some gas chromatographic

results have already been used to adjust the average absorptivity to the proportion of various olefins in automobile exhaust samples. However, this use of the gas chromatographic data does not prevent the further comparison of the absolute concentration levels from gas chromatographic analyses with the DAB analyses.

There are a number of limitations on the gas chromatographic data. The method as used permitted analysis only for two to six carbon olefins. Seven carbon and higher olefins were not determined. The sampling procedure involved collection in a plastic bag, concentration on silica gel at dry ice-acetone temperatures, desorption at 150°, and passage through ascarite. Each of these steps can result in small losses of hydrocarbons. The samples for colorimetric analysis were collected directly into a bubbler containing the DAB reagent. The principal sources of error would be interference effects. The subject will be discussed shortly.

Three analyses were made over a period of one week on diluted exhaust using the same automobile and fuel each time. The gas chromatographic analysis gave, for the sum of four, five and six carbon olefins, 9.9, 10.9, 11.6 μg/liter. The DAB method gave analyses of 14.7, 13.6 and 15.1 μg/liter. Thus, the DAB method gave results about one-third higher than the gas chromatographic analysis or on the average, 3.6 μg/liter higher. Analyses of the fuel used (saturates, 40.0; olefins, 25.2; aromatics, 34.8 mol percent) and undiluted exhaust have been reported.

For a series of fuels, five and six carbon olefin contents in the fuel were reflected in the exhaust (18). The fuel used contains 7.3 mol percent

hexenes and 4.6 mol percent heptenes (18). The heptenes were not determined in the exhaust gas analyses. These heptenes plus small amounts of exhaust gas octenes account for most of the difference between the olefin contents obtained by the DAB analysis and the gas chromatographic analysis. These facts do not prove that the two methods of analysis are in close agreement. However, the results do indicate that there are no gross discrepancies between the absolute concentrations obtainable by the gas chromatographic and colorimetric method of analysis for automobile exhaust gases.

To investigate the effects of various interferences, the exhaust gases as collected in a plastic bag directly from the exhaust system of the automobile were subjected to several procedures for removal of aromatic and oxygenated materials (Table VII). A carbowax column was used to remove aromatic hydrocarbons from the exhaust gas samples. Phenols and many oxygenated compounds also would be retained for times long compared to the olefins. Some loss of formaldehyde in the column also will occur. The saturated aqueous sodium bisulfite solution is very effective in removing formaldehyde and many other aldehydes and ketones. Other oxygenated compounds, if present in the sample, and vapor phase phenols and acid gases also will be partially removed. The 0.1 N sodium hydroxide solution should be effective in removing aldehydes and ketones. It was thought that it possibly might be more effective than the bisulfite solution in the removal of phenols and acid gases.

The bisulfite solution lowers the absorbance 10 to 20%. The previous results indicate that this is due to removal of formaldehyde. This decrease is not as great as one might anticipate from some of the data obtained with

single olefin-formaldehyde mixtures. This result probably arises from the relatively small proportion of highly reactive olefins in the exhaust. The carbowax column effects the absorbance to a rather small extent. The combination of the carbowax column and bisulfite solution is slightly more effective than the carbowax column alone for fuel No. 5. The bisulfite solution does not appear to remove much more interfering material than the carbowax column alone. The net result of clean-up by both systems is to cause the absorbance to be quite close to the absorbance without clean-up. Consequently, at least with the fuels used, the interferences appear to largely cancel each other, and the removal techniques do not appear essential.

Several samples of automobile exhaust diluted about one hundred to one with air were collected in plastic bags and analyzed for olefin (Table VIII). The samples were run with and without a bubbler containing aqueous sodium bisulfite or sodium hydroxide solution in the sampling line preceding the bubbler containing DAB reagent. In contrast to the 10 to 20% decrease found for undiluted exhaust, no really significant difference is observed when the aqueous solutions are used. It may be that the greater dilution favors reaction of the olefin with the DAB reagent rather than with the formaldehyde or other oxygenated materials.

When diluted irradiated exhaust is passed through aqueous solution prior to olefin analysis, a marked decrease in absorbance occurs (Table IX). This is true, whether the sample was collected directly into a bubbler train, or collected first into a plastic bag and subsequently passes through the bubblers.

The much greater interference experienced with irradiated exhaust probably results from the much higher formaldehyde-to-olefin ratio. In the diluted,

non-irradiated exhaust samples, the higher olefins are at a concentration of about 3 ppm by volume, while the formaldehyde are only 0.6 ppm (4). In the irradiated system the olefin are reduced to 0.5 to 1 ppm, while the formaldehyde increases to 3 ppm by volume (4). Consequently, the formaldehyde-to-olefin ratio increases from one to five up to as much as six to one. This thirty-fold change in the ratio results in a much more severe formaldehyde interference. The concentration of other aliphatic oxygenates also is considerably increased.

These results for irradiated exhaust indicate that it is essential that an aqueous absorbing solution be present in a bubbler preceding the bubbler containing the DAB reagent. This sytem also should be used in atmospheric sampling for olefins. Depending on its exact composition the aqueous solution can itself be used to provide the sample for a formaldehyde, aldehyde or carbonyl analysis.

DISCUSSION

The present method is applicable to both source and atmospheric concentrations of olefins on a quantitative basis. The earlier molybdate method of MacPhee (16) can be applied to atmospheric analysis if very large samples are used. Not only olefins, but also carbon monoxide, acetylene, acrolein, hydrogen and sulfur dioxide react with this reagent. Ozone and nitrogen dioxide also interfere. Consequently, a complex clean-up is necessary involving trapping at liquid oxygen temperature, transfer to liquid nitrogen and pumping to remove ozone and carbon monoxide, along with use of both Ascarite and Hopcalite adsorbents (16). The total procedure appeared to consume about four

hours per sample. This method does respond to ethylene and propylene, but the absorptivities cover a three to four fold range. The sensitivity is about one third that of the DAB method. Mader and Eye developed a bromometric method for vapor phase olefins which is not nearly sensitive enough for olefins in the atmospheric concentration range (17). This method does not respond to ethylene, gives 20% response to propylene, 80% response to butenes, and 90% or higher response to pentenes. Both this method and the bromocoulometric method of Nicksic (19) are subject to interferences from some sulfur compounds, phenols, and other unsaturated compounds besides olefins in the sample. The bromocoulometric method of Nicksic (19) has potential for direct atmospheric analysis but problems of bromine loss, sensing solution composition, and variations in electrode potential need further investigation. It is not clear at present how much response to ethylene and propylene occurs at low concentrations. Small water contents result in low bromine losses but also result in low bromination efficiencies for 1-alkenes. Comparison of the bromocoulometric results with gas chromatographic analyses of olefins in the 0.1 to 1 ppm range from diluted automobile exhaust showed an average difference of 30% and a number of differences of greater than 50% between the two methods (19).

The above discussion indicates the numerous problems associated with other methods for trace quantities of olefins. The present method also has many similar problems associated with its application to complex mixtures at low concentrations. However, the data presented in this investigation show that the DAB method is applicable to complex gas samples with good reproducibility and moderate accuracy. The accuracy in the simple aliphatic mixtures was about

± 5%. In automobile exhaust analysis of the various types discussed, the accuracy may not be better than ± 10 to ± 20%. This estimate is based on the uncertainities associated with the average absorptivities used and the interferences encountered. The methods discussed for removal of serious interferences are considered as being used in arriving at this estimate.

The sensitivity of the method at atmospheric concentrations is defined by the average absorptivity of 0.14 μg^{-1} ml cm^{-1}. In other terms, this means that an absorbance of 0.1 will be obtained if 50 liters of an atmospheric sample containing 0.3 µg/liter are passed through 20 ml of reagent solution. Assuming an average vapor density of 3 g./liter, this is at a level of 0.1 ppm by volume of four carbon and higher olefins. In most of the work done the olefins were collected in 20 ml of reagent. The use of 10 ml of reagent was investigated only with trans-2-butene-air mixtures. The data obtained indicated the need for more care and for the use of two bubblers in series since the collection efficiency is adversely affected. However, the sensitivity can be doubled by the reduction of sample volume from twenty to ten ml. The sensitivity for diolefins at atmospheric concentrations will be about 0.3 μg^{-1} ml cm^{-1}. Consequently, as little as 2 or 3 pphm of diolefins can be detected in the vicinity of industrial sources of diolefins.

The present method has been successfully applied to following the reaction of olefins in photolyzed automobile exhaust diluted 1000 to 1. The initial olefin concentrations were about 0.5 ppm by volume, while the olefin concentrations measured after several hours of irradiation in a dynamic system were at 0.1 ppm and below.

The need to use a different absorptivity value for different olefin concentration ranges in the gas sample usually should present no problem. Even when the olefin composition and concentration is totally unknown, a preliminary analysis will give the approximate concentration. This data can then be used to chose the appropriate absorptivity in terms of 1-butene.

The reaction conditions in the present method have been adjusted to minimize the reaction of propylene. Propylene can be determined with good sensitivity under other conditions (Table VII). Consequently, a modification of the present method might prove useful in determining propylene in gas mixtures which do not contain higher olefins.

The present method cannot replace other methods of analysis, particularly gas chromatography. However, it should prove valuable in the absence of other analytical tools for determining trace quantities of olefins. It can serve as a useful complementary method to gas chromatography in many air pollution and industrial hygiene problems.

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LIST OF FIGURES

Figure 1. Absorption Spectra of 1,3-Butadiene and Isobutylene Products with Dimethylaminobenzaldehyde.

TABLE I. ABSORPTIVITIES OF SOME BUTENE REACTION PRODUCTS

Olefin	Concn., ppm	Ratio of DAB to H_2SO_4 soln.	Reaction time in H_2SO_4 Hr.	Absorptivities μg^{-1} ml cm^{-1} at 500 mμ for various reaction times after addition of DAB solution, in minutes. 30	45	60	120
cis-2-butene	12.5	80/1	1 3/4	0.08	0.09	0.10	0.11
		57/1		.11	.12	.12	.14
		40/1		.13	.14	.15	.15
		27/1		.12	.13	.13	.13
		20/1		.11	.11	.11	.11
1-butene	12.5	133/1	1 3/4	.02	.02	.03	.04
		80/1		.03	.04	.05	.06
		57/1		.05	.06	.06	.07
		40/1		.06	.06	.07	.07
		27/1		.05	.05	.05	.05
		20/1		.04	.04	.04	.04
isobutylene	12.5	133/1	1 1/4	.47	.53	.58	.60
		80/1		.72	.73	.70	.62

Table I. cont.

Olefin	Concn., ppm	Ratio of DAB to H_2SO_4 soln.	Reaction time in H_2SO_4 Hr.	Absorptivities μg^{-1} ml cm^{-1} at 500 mμ for various reaction times after addition of Dab solution, in minutes. 30	45	60	180
		57/1		.70	.68	.65	.55
		40/1		.58	.54	.50	.38
		27/1		.35	.33	.33	.32
		20/1		.32	.31	—	--

TABLE II. ABSORPTIVITIES OF UNHEATED REACTION PRODUCTS

Olefin	Concn. in ppm by volume	Reaction time, minutes	Absorptivities at 500 mμ at various ratios of DAB to H_2SO_4 soln., μg^{-1} ml cm^{-1} 1/4	1/8	1/20	1/40	1/80
propylene	25	15	0.002	0.01	0.005	--	--
		60	.006	.03	.02	--	--
		120	--	.05	.03	.03	.002
1-butene	12.5	15	--	.07	.03	--	--
		60	.20	.10	.12	.03	.02
		120	.22	.13	--	.06	.04
cis-2-butene	12.5	15	.12	.06	.02	--	--
		60	.12	.07	.04	--	.01
		120	.11	.08	.06	--	.03
isobutylene	12.5	15	.75	.68	.35	--	--
		60	.69	.59	--	--	.12
		120	.58	.54	--	--	.20
1,3-butadiene	12.5	60	--	--	--	--	.21
		120	--	--	--	--	.22

TABLE III. ABSORPTIVITIES OF SOME HEATED OLEFIN PRODUCTS AT VARIOUS VOLUME RATIOS OF DAB TO SULFURIC ACID SOLUTIONS

Olefin	Concn., in ppm by volume	Heating Period,[a] minutes	Absorptivities at 500 mμ for ratios of DAB to H_2SO_4 soln., μg^{-1} ml cm^{-1} 1/4	1/8	1/40	1/80
ethylene	500	5	--	--	0.002	0.002
		15	--	--	.002	.002
		20	--	--	.002	.002
propylene	25	5	0.06	0.14	.03	.01
		10	.05	.11	.03	.01
		15	.05	.09	.03	.01
	250	5	--	--	.015	.004
		15	--	--	.01	.0035
		20	--	--	.01	.003
1-butene	12.5	5	.13	.27	.19	.10
		10	.13	.24	.18	.10
		15	.10	.25	.17	.12
trans-2-butene	12.5	5	--	--	.18	.12
		10	--	--	.18	.11
		15	--	--	.17	.13
isobutylene	12.5	5	--	.43	.40	.34
		10	--	.32	.26	.22
		15	--	--	.21	.20

Table III cont.

Olefin	Concn., in ppm by volume	Heating Period,[a] minutes	Absorptivities at 500 mμ for ratios of D/B to H_2SO_4 soln., μg^{-1} ml cm^{-1} 1/4	1/8	1/40	1/80
1,3-butadiene	12.5	5	--	--	.35	.28
		10	--	--	.25	.22
		15	--	--	.23	.23
		20	--	--	.20	.21
2-methyl-2-butene	11.5	5	--	--	.12	.10
		15	--	--	.10	.09
		20	--	--	.12	.08

a Heated at 100° for indicated time period

TABLE IV. ABSORPTIVITIES FOR HEATED PRODUCTS OF OLEFINS AT

1/80 RATIO OF DAB REAGENT TO SULFURIC ACID

Olefin	Concn in ppm by volume	Absorptivities, μg^{-1} ml cm-1 15 minute heating	20 minute heating
ethylene	500	0.001	0.001
propylene	250	0.003	0.003
propadiene	100	0.002	0.002
1-butene	1	0.165±0.015	0.15±0.01
	12.5	0.125±0.01	0.11±0.003
	50	0.10	0.09
cis-2-butene	1	0.19±0.02	0.18±0.02
	12.5	0.14±0.01	0.12±0.01
trans-2-butene	1	0.18±0.04	0.17±0.035
	12.5	0.13	0.13
isobutylene	1	0.33±0.04	0.25±0.03
	12.5	0.20±0.02	0.15±0.02
	25	0.195	0.165
1,3-butadiene	1	0.35±0.02	0.30±0.02
	12.5	0.23	0.21
	50	0.19±0.025	0.17±0.02
1-pentene	11	0.105±0.008	0.10±0.008
cis-2-pentene	1	0.11±0.01	0.10±0.01
	11	0.09	0.08
2-methyl-1-butene	11	0.10±0.015	0.10±0.015

Table IV. cont.

Olefin	Concn. in ppm by volume	Absorptivities, μg^{-1} ml cm^{-1} 15 minute heating	20 minute heating
2-methyl-2-butene	1	0.10±0.01	0.10±0.015
	11.5	0.08	0.08±0.01
2-methyl-1,3-butadiene	12	0.20±0.04	0.21±0.035
1-hexene	0.9	0.09±0.01	0.09±0.01
	9.5	0.085±0.005	0.085±0.005
2-methyl-1-pentene	10	0.07±0.01	0.07±0.01
2-methyl-2-pentene	10	0.08	0.08

TABLE V. ANALYSES FOR OLEFIN CONTENT OF HYDROCARBON MIXTURES

Mixture	Reaction time, minutes	Hydrocarbon concn., ppm Total	Olefin	Absorbance (500 mμ) Exptl.	Calcd.	Calcd. Olefin concn., ppm
36	15	0.58	0.22	0.32±0.03[a]	0.34 [f]	0.23
	20			0.32±0.02	0.29	0.20
37	15	0.24	0.20	0.16±0.04[b]	0.16 [f]	0.20
	20			0.16±0.05	0.14	0.18
36	15	2.62	1.00	0.39±0.03[c]	0.37 [f]	0.95
	20			0.37±0.03	0.32	0.87
37	15	1.21	1.00	0.38±0.03[c]	0.40 [f]	1.05
	20			0.36±0.04	0.35	0.97
37	15	12.1	10.0	0.48±0.07[d]	0.46 [g]	9.6
	20			0.43±0.07	0.41	9.5
37	15	121	100	0.47±0.05[e]	0.46 [g]	98
	20			0.43±0.03	0.41	95

a 60 liter sample collected at 1 liter/minute

b 30 liter sample collected at 0.5 liter/minute

c 15 liter sample collected at 0.5 liter/minute

d 2.5 liter sample collected at 0.5 liter/minute

e 0.25 liter sample collected at 0.05 liter/minute

f calcd. using 1 ppm calibration data for individual olefins (Table IV)

g calcd. using 12.5 ppm calibration data (Table IV)

TABLE VI. ANALYSIS OF OLEFIN-AROMATIC HYDROCARBON MIXTURES

Olefin	Aromatic	Concn., ppm by vol. Olefin	Concn., ppm by vol. Aromatic	Calculated olefin concn., ppm by vol. [a]
1-butene	benzene	25	140	26
	toluene	25	115	26
	p-xylene	25	100	27
	o-xylene	25	100	24
	m-xylene	25	100	25
isobutylene	benzene	25	140	21
	toluene	25	115	17
	p-xylene	25	100	18
	o-xylene	25	100	17
	m-xylene	25	100	10
1,3-butadiene	benzene	50	140	9
	toluene	25	115	10
	p-xylene	50	195	15
	o-xylene	50	200	18
	m-xylene	50	200	12

[a] Calculated from observed absorbances and data in Table IV.

TABLE VII. EFFECTS OF REMOVAL OF AROMATICS AND OXYGENATES FROM AUTOMOBILE EXHAUST ON DETERMINATION OF OLEFINS BY DAB METHOD

Fuel Used	Removal Technique	Absorbance (500 mμ)	Relative Response [c]
No. 3 [a]	none	1.88	1.00
	satd. $NaHSO_3$ soln.	1.72	0.92
	carbowax column	2.00	1.06
	satd. $NaHSO_3$ soln. and carbowax column	2.00	1.06
No. 3 [a]	none	1.72	1.00
	satd. $NaHSO_3$ soln.	1.47	0.85
	0.1 N NaOH soln.	1.46	0.85
No. 5 [b]	none	1.90	1.00
	satd. $NaHSO_3$ soln.	1.45	0.79
	carbowax column	2.05	1.08
	satd. $NaHSO_3$ soln. and carbowax column	1.94	1.02

a Saturates, 44.8 mol %; Olefins, 18.1 mol %; Aromatics 37.1 mol %

b Saturates, 40.0 mol %; Olefins, 25.2 mol %; Aromatics 34.8 mol %

c Response for samples subjected to no pre-treatment set equal to 1.00.

TABLE VIII. EFFECTS OF REMOVAL OF OXYGENATED MATERIAL FROM DILUTED AUTOMOBILE EXHAUST GASES ON DETERMINATION OF OLEFINS BY DAB METHOD

Fuel Used	Removal Technique	Absorbance (500 mμ)	Relative Response [c]
No. 3 [a]	none	0.59	1.00
	satd. $NaHSO_3$ soln.	0.64	1.08
No. 3 [a]	none	0.73	1.00
	satd. $NaHSO_3$ soln.	0.75	1.03
	0.1 N NaOH soln.	0.74	1.01
No. 5 [b]	none	0.72	1.00
	0.1% $NaHSO_3$ soln.	0.70	0.97

a Saturates, 44.8 mol %; Olefins, 18.1 mol %; Aromatics, 37.1 mol %

b Saturates, 40.0 mol %; Olefins, 25.2 mol %; Aromatics, 34.8 mol %

c Response for samples subjected to no pre-treatment set equal to 1.00

TABLE IX. EFFECTS OF REMOVAL OF OXYGENATED MATERIAL FROM DILUTED, IRRADIATED EXHAUST GASES ON DETERMINATION OF OLEFINS BY D4B METHOD

Fuel Used	Removal Technique	Absorbance	Relative Response
No. 3 [a]	none	0.34 [b]	1.00
	water	0.18 [b]	0.53
No. 3 [a]	none	0.25 [c]	1.00
	water	0.11 [c]	0.44
	satd. $NaHSO_3$ soln.	0.10 [c]	0.40

a Saturates, 44.8 mol %; Olefins, 18.1 mol %; Aromatics, 37.1 mol %

b Samples collected directly from line into bubbler train

c Sample collected in plastic bag

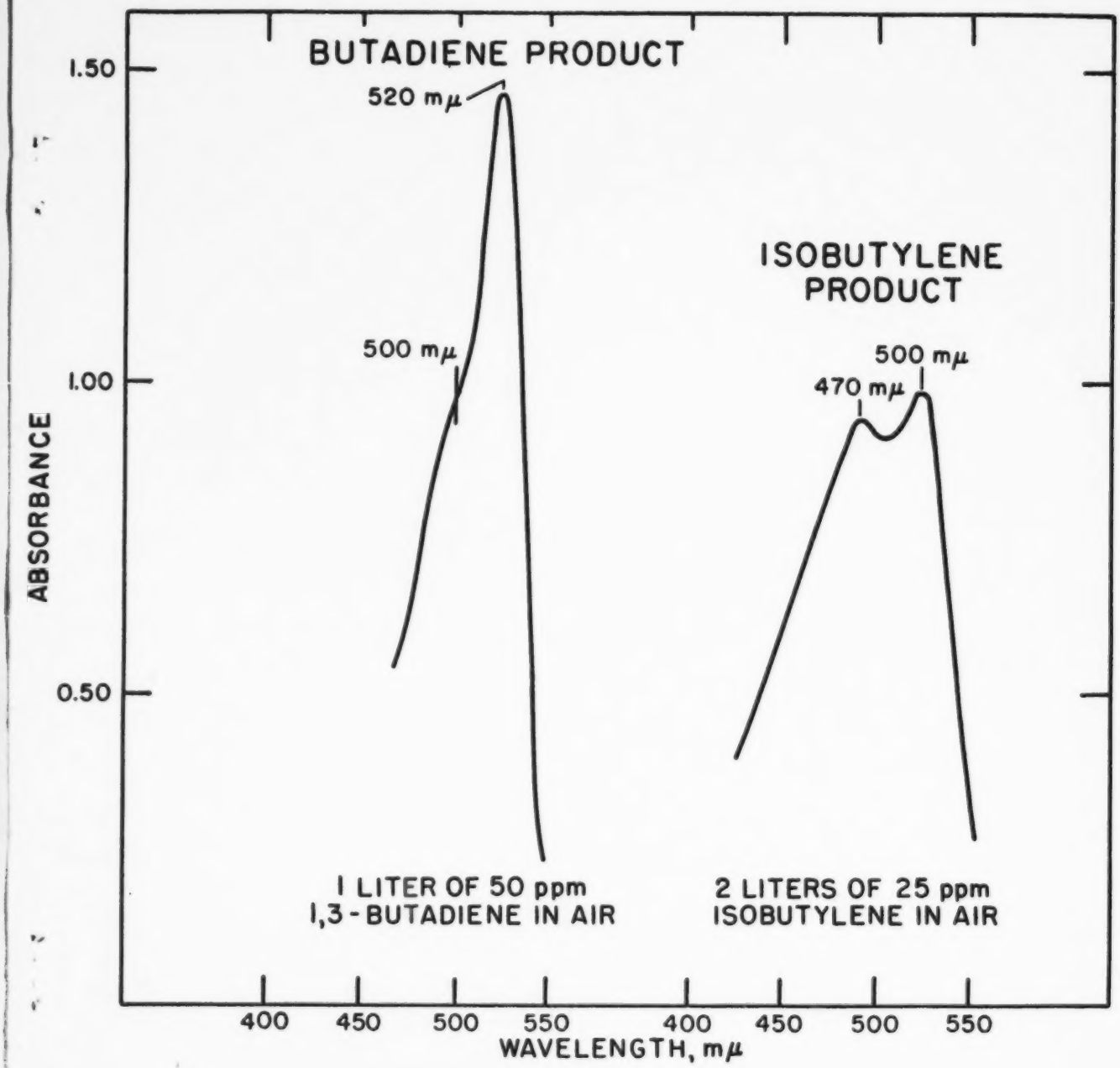
BUTADIENE PRODUCT
520 mμ
500 mμ
ISOBUTYLENE
PRODUCT
500 mμ
470 mμ
1.50
1.00
0.50
ABSORBANCE
1 LITER OF 50 ppm
1,3 - BUTADIENE IN AIR
2 LITERS OF 25 ppm
ISOBUTYLENE IN AIR
400
450
500
550
400
450
500
550
WAVELENGTH, mμ

FIGURE 1